COMMUNICATIONS

Addition of Hydrogen Bromide to Allenes

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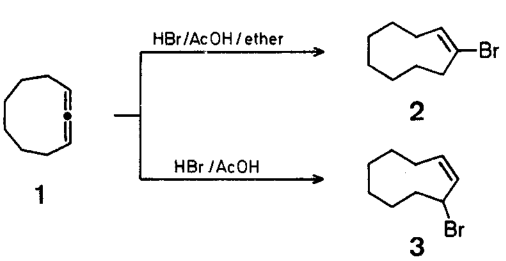
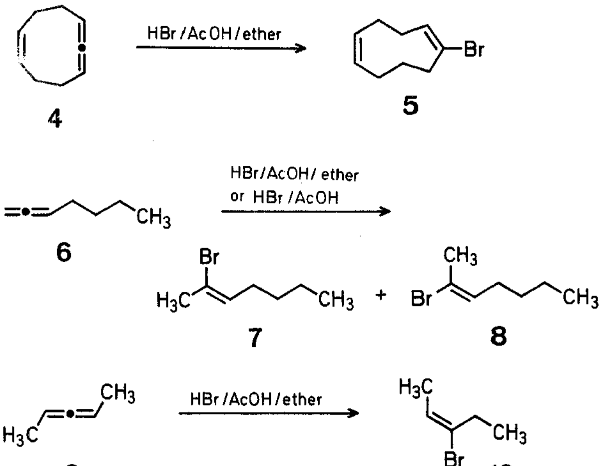
There are reports in the literature that addition of hydrogen bromide to allenes, under conditions which favour both radical[1] and ionic[2] reactions, leads to products in which the bromo-substituents are attached to what were originally the central carbon atoms of the allenic systems. We were therefore not surprised when we found, several years' ago, that treatment of an ethereal solution of cyclonona-1,2-diene (**1**) with a small excess of hydrogen bromide/acetic acid gave 1-bromo-*cis*-cyclononene (**2**), in high yield, as virtually the sole product[3]. Some two years after the publication of our work, Nagendrappa et al. reported that when **1** was treated with a stoichiometric amount of hydrogen bromide/acetic acid (45%, w/v) *in the absence of other solvent*, 3-bromo-*cis*-cyclononene (**3**) was obtained in high yield[4]. The latter product **3** clearly results when the bromo-substituent becomes attached to what was originally one of the end carbon atoms of the starting allene **1**.



Although it was clear from the published N.M.R. data that our original conclusion was correct, Nagendrappa et al. appeared to question its validity and not to consider the possibility that solvent might have a profound effect on the addition of hydrogen bromide to cyclonona-1,2-diene (**1**). We now report that this is indeed the case and that when a solution of **1** in ether or petroleum ether (b.p. 30–40°) is treated with an excess of hydrogen bromide/acetic acid at room temperature, 1-bromo-*cis*-cyclononene (**2**) is obtained, in high yield, as virtually the sole product[5]. We have also confirmed that 3-bromo-*cis*-cyclononene (**3**) is the major product when the reaction is carried out in the absence of additional solvent and that no 1-bromo-*cis*-cyclononene (**2**) is then obtained.

Treatment of an ethereal solution of cyclonona-1,2,6-triene (**4**) with hydrogen bromide/acetic acid gives 1-bromo-*cis,cis*-cyclonona-1,5-diene (**5**)[6], in high yield, as virtually the sole product. More interestingly, hepta-1,2-diene (**6**) reacts with hydrogen bromide/acetic acid *both in the absence of additional solvent and in ether solution* to give a mixture of the (*Z*)- and (*E*)-isomers of 2-bromohept-2-ene[7] (**7** and **8**, respectively) as virtually the sole products. These products again result from the attachment of the bromo-substituent to what was originally the central carbon atom of the starting allene **6**. We had previously observed that penta-2,3-diene (**9**) reacted with hydrogen bromide/acetic acid in ether solution to give mainly one geometrical isomer of 3-bromopent-2-ene (probably **10**)[8].



The main purposes of the present report are to clarify an apparent contradiction in the literature and to give some examples of a potentially useful reaction. No attempt will be made to rationalize the above results here. However, it is relevant to add that if the reactions which take place in the presence of added solvent occur by ionic mechanisms, protonation on the terminal carbon atoms of the allenic systems (to give incipient vinyl cations) must be favoured over protonation on the central carbon atoms to give cations which, following rotation, can acquire allylic stabilization.

1-Bromo-*cis,cis*-cyclonona-1,5-diene (5):

Hydrogen bromide/acetic acid (45% w/w, 1.30 g, 7.2 mmol hydrogen bromide) was added over a period of 2 min to a stirred solution of cyclonona-1,2,6-triene (0.50 g, 4.2 mmol) in ether (10 ml) at 20°. The reactants were stirred for a further period of 15 min and then extracted with saturated aqueous sodium carbonate (2 × 10 ml) and water (10 ml). The dried ($MgSO_4$) ether layer was evaporated under reduced pressure to give a pale yellow oil (0.72 g, 86%). The latter material was shown (G.L.C., 5′ SE 30 column, 100°) to contain one major component which was isolated pure by preparative G.L.C. (5′ SE 30 column, 100°) and shown to be identical to authentic 1-bromo-*cis,cis*-cyclonona-1,5-diene[6].

^{1}H-N.M.R. (220 MHz, CCl_4): $\delta = 6.11$ (t, 1 H, $J = 8.5$ Hz), 5.68 (dt, 1 H, $J = 8.5$ and 11 Hz), 5.38 (dt, 1 H, $J = 8.5$ and 11 Hz), 2.38 (m, 2 H), 2.01 (m, 6 H), 1.72 ppm (m, 2 H).

Addition of Hydrogen Bromide to Hepta-1,2-diene[9] (6):

Method A: Hydrogen bromide/acetic acid (45% w/w, 1.30 g, 7.2 mmol hydrogen bromide) was added over a period of 2 min to a stirred solution of hepta-1,2-diene (0.50 g, 5.2 mmol) in ether (10 ml) at 20°. The reactants were stirred for a further period of 15 min and then worked-up as above to give a yellow oil (0.60 g, 66%). The latter material was shown by G.L.C. (5′ SE 30 column, 100°) to contain two components in the proportions of ~3:1 with the shorter R_T component predominating. Both components were isolated in a pure state by preparative G.L.C.

The major component was identified as (*E*)-*2-bromohept-2-ene* (**8**):

^{1}H-N.M.R. (CCl_4): $\delta = 5.56$ (tq, 1 H, $J = 7$ and 1.2 Hz), 2.3 (s, 3 H), 2.2 (m, 2 H), 1.5 (m, 4 H), 1.0 ppm (m, 3 H).

I.R. (film): $\nu_{max} = 1630$ (w), 1660 (m) cm^{-1}.

Mass spectrum (70 eV): $m/e = 176.0197$ ($M^{\oplus}$), calc. for $C_7H_{13}Br$ 176.0201.

The minor component was identified as *(Z)-2-bromohept-2-ene* (**7**):

^{1}H-N.M.R. (CCl_4): $\delta = 5.80$ (tq, 1 H, $J = 8$ and 1 Hz), 2.2 (s, 3 H), 2.0 (m, 2 H), 1.35 (m, 4 H), 0.9 ppm (m, 3 H).

I.R. (film): $\nu_{max} = 1650\ cm^{-1}$.

Mass spectrum (70 eV): $m/e = 176.0199$ ($M^{\oplus}$).

Method B: Hydrogen bromide/acetic acid (45% w/w, 1.30 g, 7.2 mmol hydrogen bromide) was added over a period of 2 min to stirred hepta-1,2-diene (0.50 g, 5.2 mmol) at 0° (ice-bath). The reaction was slightly exothermic. The reactants were stirred for a further period of 30 min and then worked-up as above to give a colourless oil; yield: 0.73 g (81%); which was shown (G.L.C., N.M.R.) to contain only (*Z*)- and (*E*)-*2-bromohept-2-enes* [(**7**) and (**8**), respectively] in the relative proportions of ~1:5.

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[4] G. Nagendrappa, P. Mohanakrishnan, G. Mehta, D. Devaprabhakara, *Chem. Ind. (London)* **1971**, 850.
See also S. N. Moorthy, A. Singh, D. Devaprabhakara, *J. Org. Chem.* **40**, 3452 (1975).

[5] When the addition is carried out very slowly (over ~18 h) an additional product, 2,3-dibromo-*cis*-cyclononene, identical to an authentic sample[3], is obtained in addition to **2**.

[6] M. S. Baird, C. B. Reese, *J. Chem. Soc.* [C] **1969**, 1808.

[7] The (*Z*)- and (*E*)-isomers (**7** and **8**, respectively) are formed in the relative proportions of 1:5 in the absence and 1:3 in the presence of ether. As H-3 of the major isomer ($\delta = 5.56$ ppm) resonates at higher field than H-3 of the minor isomer ($\delta = 5.8$ ppm), it is reasonable to conclude [S. W. Tobey, *J. Org. Chem.* **34**, 1281 (1969)] that the (*E*)-isomer (**8**) predominates.

[8] M. S. Baird, *Ph. D. Thesis*, Cambridge University, 1968, p. 205.

[9] Initial experiments were carried out by Mr. A. McGown.